On-Site Pilot-Scale Demonstration of a Low-Cost Biological Process for the Treatment of High-Sulphate Mine Waters

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Abstract

This paper describes the commissioning and operation of a pilot-scale passive biological sulphate reduction (BSR) process, treating mine-impacted water from a South African coal mine. The pilot plant comprises three 7 m³ reactors, with a nominal feed rate of 245 L/d. The substrate comprises woodchips, wood shavings, hay, lucerne and cow manure. Process performance is evaluated relative to influent pH level, hydraulic residence time (HRT), ambient temperature variations, and substrate replenishment rate.

Early results demonstrate removal of sufficient sulphate to meet regulatory requirements for discharge or agricultural use. Benchmark capital and operating cost estimates of the process are discussed.

Keywords: passive treatment, biological sulphate reduction, mine waters, pilot plant

Introduction

The threat to the South African environment from acid mine drainage and mine-impacted waters is well documented. Effluents from the South African gold- and coal-mining industries can severely impact upon the quality of water supplies, both during the mines' operating lives and after their closure. Many such operations are nearing the ends of their operating life-cycles, and suitable processes for the post-closure treatment of decants and seepages are urgently required. These acidic, sulphate-laden and metal-contaminated waters are typically treated by lime neutralisation, which removes the metals and increases the pH level, but has little impact on the sulphate level. In South Africa, stringent regulations enforce low sulphate discharge limits of 200 600 mg/L. Biological treatment using sulphate-reducing bacteria is being investigated as an alternative to conventional technologies for the treatment of mine-impacted effluents. A passive process, with relatively low capital and operating costs, is ideally suited to post-closure applications, and laboratory-scale test work has demonstrated that it can meet the regulatory sulphate discharge limits.

Previous laboratory-scale test work (Neale *et al*. 2017) demonstrated that over 95 % of the sulphate in acidic mine-impacted waters laden with around 3 000 mg/L of sulphate could be removed in a passive BSR process, at an HRT of 4 days. The pH levels of the waters increased to around 7, residual metals were precipitated, and effluent sulphate concentrations of between 90 and 140 mg/L were achieved. It was also shown that residual sulphide and manganese in the BSR effluent could be removed using a two-stage process comprising an oxidation pond and a pebble-bed pond. Significant reductions in the ammonium, bicarbonate, phosphate and calcium levels, and minor reductions in the magnesium and potassium levels, were also achieved.

Based on these results, a pilot plant was designed and constructed. The plant was designed conservatively, with an HRT per stage of 6 days, at a feed rate of 245 L/d, giving a plant comprising three reactors with an active volume of around 7 m³ each. This paper describes the commissioning and early operation of the pilot plant, which was installed next to a raw water dam at a South African coal mine in Mpumalanga Province, South Africa. The acidic, sulphate-laden raw water from the dam is fed to the BSR plant, and the treated effluent is returned to the dam.

Pilot Plant Commissioning

To facilitate plant start-up, a suitable inoculum of around 6 000 L was prepared at Mintek. The substrate, consisting of a mix of woodchips, wood shavings, hay, lucerne and kraal manure, was blended at Mintek and loaded into 1 m3 bulk bags. These pre-prepared materials, together with the pilot plant equipment, were transported to the site, and the equipment was installed. Commissioning included loading of the vessels with a layer of pebbles and the pre-mixed substrate, and introducing the pre-prepared inoculum, which took place on 15 September 2017.

A crane was used to load the vessels. The pebbles were loaded first, by placing bulk bags in the open vessels, cutting the bags open, and then lifting the bags out. Each vessel was filled with 1 000 kg of pebbles, which was sufficient to cover the outlet box at the base of each vessel. The pre-mixed substrate was loaded in a similar way. Bulk bags containing the substrate were lifted by crane and positioned in the vessels, the bags were cut open, and then lifted out of the vessels.

In an attempt to promote rapid inoculation and start-up of the plant, some of the bags of pre-mixed substrate were contacted with inoculum prior to being transported to the site. The bags were dipped into one of the inoculum containers, and then lifted out and drained. The pre-wetted substrate was added to Reactor 1, since it was considered that a fast start-up in Reactor 1 would promote faster commissioning of the process once a feed was applied.

Following the loading of the substrate, a mixture of pre-prepared inoculum and raw water was pumped into the vessels, in an approximate ratio of 70 % inoculum to 30 % raw water. At the time of inoculating the plant, the pH level of the raw water was around 2.85, and so the 70:30 ratio of inoculum to raw water was chosen to ensure that the pH level was not too low. Small quantities of nutrients (ammonium sulphate and phosphoric acid) were added to the vessels to promote bacterial growth.

As the vessels were filled, it was discovered that there was a leak in the pipework of Reactor 2, and so the inoculation of Reactor 2 was postponed. In addition, it was noted that the quantity of substrate and fluid that had been added to Reactors 1 and 3 was not sufficient to completely fill the vessels. Following the loading and inoculation of the vessels, they were allowed to stand for a period of several weeks to enable the inoculum to take effect, and to observe whether any expansion or contraction of the substrate beds took place.

Two weeks after the loading and inoculation of the vessels, the first set of routine measurements was undertaken in Reactors 1 and 3 (on 29 September 2017), as summarised in tab. 1.

These results clearly show the beneficial impact of the pre-wetted substrate mixture in Reactor 1. The low redox potential and high pH level in that vessel indicated that bacterial activity had been established in Reactor 1, but was not yet apparent in Reactor 3. The much lower sulphate concentration of 1.36 g/L in Reactor 1 compared to Reactor 3 confirmed that biological sulphate reduction activity had been established in this vessel.

Table 1. *Initial routine measurements in Reactors 1 and 3, two weeks after inoculation*

Reactor	Temperature (°C)	Redox potential (mV, Ag|AgCl)	pH level	Electrical conductivity (mS/cm)	$[SO_4^{2-}]$ (g/L)
1	20.0	333	6.85	10.60	1.36
3	19.7	190	3.02	10.82	5.11

On this day, the leak in Reactor 2 was repaired, in preparation for inoculating the vessel four days later, on 3 October 2017, when a mixture of inoculum, raw water and small amounts nutrients was introduced to Reactor 2. The ratio of inoculum to raw water was increased to 90:10, to try and alleviate the impact of the low pH level of the raw water. Additional quantities of inoculum and raw water were also added to Reactors 1 and 3. A second set of routine measurements was undertaken in Reactors 1 and 3, as summarised in tab. 2.

These measurements indicated that the conditions in Reactor 3 were improving, with the redox potential declining and the pH rising, albeit slowly. The increased sulphate concentration in Reactor 1 was caused by the introduction of a fresh quantity of raw water to this vessel.

The feed pump was commissioned, and recirculation from the bottom to the top of Reactor 1 was initiated, to facilitate mixing of the fluid in this vessel.

Three days later, on 6 October 2017, a further large quantity of inoculum was added to Reactor 2, together with a small quantity of raw water. The routine measurements are summarised in tab. 3.

Rapid biological sulphate reduction, facilitated by the introduction of fluid recirculation in the vessel, had occurred in Reactor 1, with the sulphate concentration declining to below 1 g/L. The sharp decline in the electrical conductivity also indicated to a high level of activity in this vessel. The benefit of introducing a smaller volume of raw water in Reactor 2 was apparent from the favourable redox potential and pH level measurements, indicating that biological activity had been initiated in this vessel within three days of inoculation. In Reactor 3, the redox potential was slowly declining, the pH level was slowly rising, but the sulphate concentration remained high.

Over the following weeks, intermittent feeding of the process was undertaken by periodically pumping 200 L batches of raw water into Reactor 1, and allowing it to overflow into Reactors 2 and 3 in order to fill them. This was done on three occasions between 27 October and 10 November 2017. By 15 November 2017, the conditions in the three vessels were as summarised in tab. 4, and on this day, 61 days after introduction of the first inoculum, continuous feed to the plant was initiated at a rate of 97.9 L/d, giving a HRT in each reactor of 15.8 d.

Table 2. *Second set of routine measurements in Reactors 1 and 3*

Reactor	Temperature (°C)	Redox potential (mV, Ag|AgCl)	pH level	Electrical conductivity (mS/cm)	[SO_4^{2-}] (g/L)
1	-	343	6.89	10.51	5.79
3	-	50	3.61	10.41	6.66

Table 3. *Third set of routine measurements in Reactors 1, 2 and 3*

Reactor	Temperature (°C)	Redox potential (mV, Ag|AgCl)	pH level	Electrical conductivity (mS/cm)	[SO_4^{2-}] (g/L)
1	20.8	345	6.68	8.94	0.912
2	20.3	275	6.32	10.81	1.83
3	18.9	34	3.93	10.56	6.70

Table 4. *Routine measurements in Reactors 1, 2 and 3 prior to start of continuous operation*

Reactor	Temperature (°C)	Redox potential (mV, Ag|AgCl)	pH level	Electrical conductivity (mS/cm)	[SO_4^{2-}] (g/L)
1	25.0	355	7.17	7.91	0.265
2	22.9	359	6.90	7.99	0.209
3	24.8	251	6.35	9.09	3.27

Figure 1 A view of the installed biological sulphate reduction pilot plant

The pH level of the raw water from the storage dam remained low, and so a mixing tank was installed to facilitate adjustment of the pH levels using lime. Raw water is pumped into the tank, where lime is added manually to raise the pH to the desired level. Once that is achieved, the mixing is stopped, the sludge is settled, and the clear water is pumped into the feed tanks.

The pilot plant is shown in fig. 1. This shows the feed vessels (partially obscured on the left), the three reaction vessels in the centre, a downstream treatment plant and the product collection vessels on the right, and the lime neutralisation tank at centre right, in front of Reactor 3

Pilot Plant Operation

Following the start of the continuous feed to the process on day 61, the objective was to increase the throughput to obtain a HRT in the first reactor of 7 days, and then to maintain that feed rate for some time. The feed rate to the plant, as well as the HRT in Reactor 1, is shown in fig. 2. The flow rate is shown in three ways: based on the feed pump setting, on the measured feed volume, and on the measured product volume. Occasional blockages were experienced in the feed line, which accounts for the scatter in the measured data.

Treated effluent first emerged on day 73 (27 November 2017). The feed flow rate was increased to the target of 220.3 L/d by 21 December 2017 (day 97), giving an HRT in Reactor 1 of 7.0 days.

The routine measurements that have been made since the start of the plant operations are shown in fig. 3, comprising the temperatures, pH levels, redox potentials, electrical conductivities and sulphate concentrations. The calculated sulphate removal levels are also shown in fig. 3.

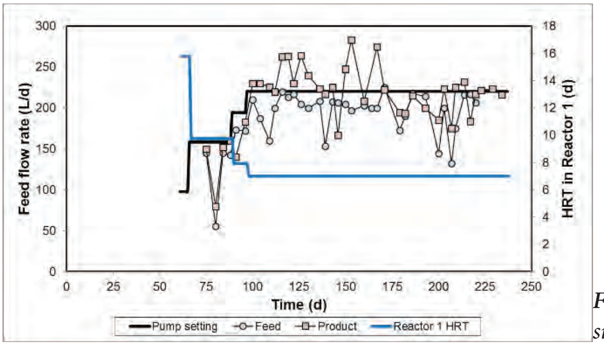

Figure 2 Feed flow rate to the on-site pilot plant

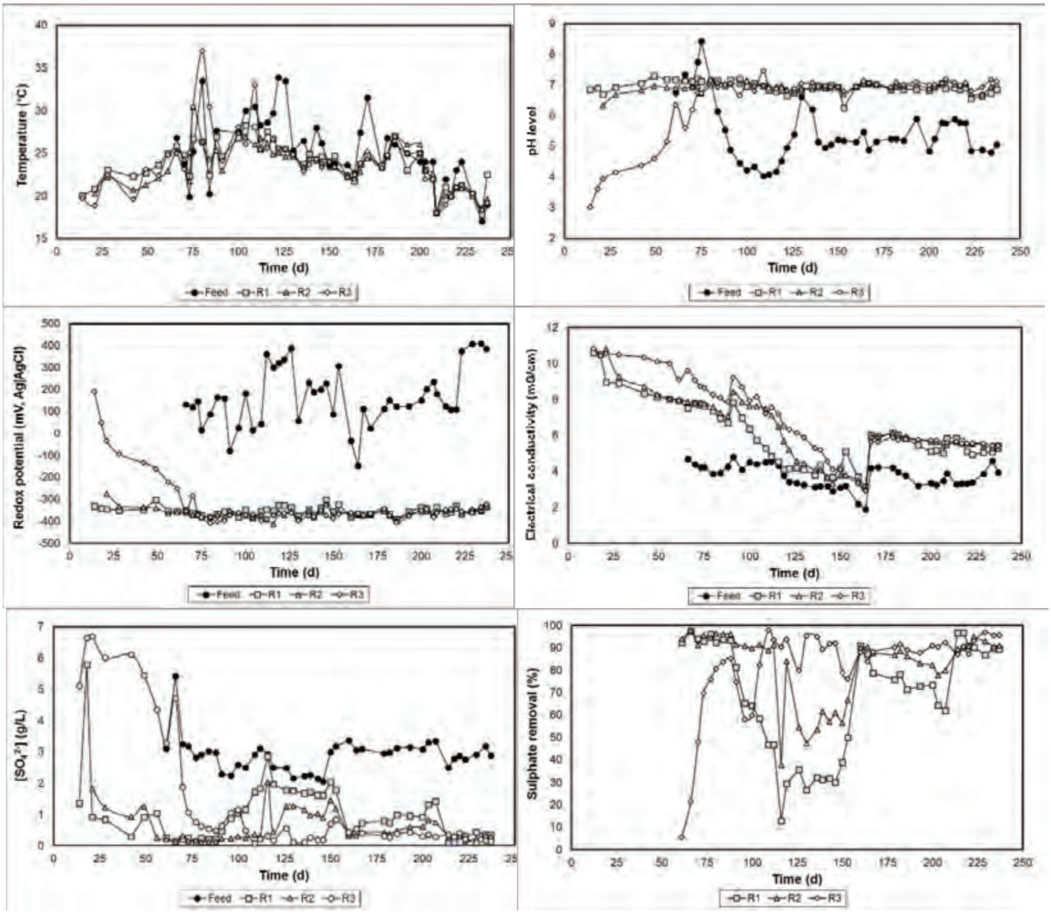

***Figure 3** Performance of the on-site pilot plant*

Following the introduction of continuous feeding on day 61, and the subsequent ramp-up of the feed rate between days 66 and 97, the following observations can be made:

- The temperatures varied quite widely, reflecting the warm conditions that are typical in summer. Generally, the temperatures remained between 25 and 30 °C through the summer months, but have begun to fall recently with the onset of autumn.
- The pH level of the feed was initially high, at around 7, owing to over-addition of lime in the pre-neutralisation tank. The current target for the pH level of the feed is 5.
- The pH levels in all three BSR reaction vessels have been maintained in the region of 7.
- The redox potentials in all three BSR reaction vessels have been maintained within a range of between 350 and 380 mV vs Ag|AgCl, which is considered ideal for the BSR process.
- The electrical conductivities in all three vessels continued to decrease after the continuous feed was applied, and the rate of decrease increased as the feed rate was ramped up. By this time, the substrate beds in all three vessels had expanded to such an extent that it was not possible to gain access to the water surface in Reactor 1 to initiate replenishment of the fast-reacting components of the substrate. Partial access to the surface was eventually possible on day 119 (12 January 2018), and substrate replenishment was initiated on that day. On day 150 (12 February 2018), the substrate replenishment regime was modified by reducing the quantity of

kraal manure being added, and introducing the addition of lucerne pellets, to mirror the substrate replenishment schedule that was implemented in the laboratory-scale test work. Limited availability of the substrates on site meant that the substrate replenishment regime was not steady during April 2018, but regular replenishment has now been instituted and will be maintained. The replenishment schedule is detailed in tab. 5.

On day 153, an increase in the electrical conductivity was observed, but it subsequently declined again. However, it is suspected that the electrical conductivity meter that was in use at that stage developed a fault, and so the measurements taken between then and day 167, when a new meter and probe were utilised, should be disregarded. The latest indications are that the electrical conductivities have stabilised in the region of 5−6 mS/cm in all three vessels.

- The average sulphate concentration of the feed to the plant has been around 3 g/L, and it has varied between about 2.0 and 3.5 g/L.
- Sulphate concentrations as low as 120 130 mg/L were recorded in Reactor 2 between days 80 and 88, corresponding to a sulphate removal of over 95 %. However, as the feed rate was increased, and prior to the introduction of a substrate replenishment regime on day 119, the sulphate concentrations in both Reactor 1 and Reactor 2 began to increase. Encouragingly, however, the sulphate concentration in Reactor 3 remained low, with the overall sulphate removal in the three-stage system remaining above 90 %.
- Following the introduction of substrate replenishment on day 119, there was a noticeable improvement in the overall performance, but this declined as the substrate replenishment was irregular. With more regular replenishment, the sulphate concentrations in all three vessels have stabilised at around 350 mg/L in Reactor 1 and about 130 mg/L in Reactor 3, corresponding to sulphate removal efficiencies of between 90 and 96 %. The system is now reaching a steady operating condition, which will enable the baseline performance under the current feed condition to be established.

The results of the on-site pilot plant operation presented here are preliminary, since the operation of the plant is still in the early stages. Future plans for the operation of the pilot plant include the following:

- Continuing the operation under the current feed rate to establish a baseline performance.
- Increasing the feed rate to establish the impact on the process performance.
- Reducing the feed pH to a level of around 4 to establish the impact on the process performance.
- Operation through the winter months to establish the impact of colder ambient temperatures on the process performance.
- Optimisation of the rate of replenishment of the fast-reacting components of the substrate. The possibility of utilising other solid and possibly liquid substrates may be investigated and evaluated with respect to the operating cost and operability of the passive BSR process.
- Evaluation of the microbiological components in the BSR process, to develop an understanding of how these components respond to changes in the feed conditions,

Table 5. *Schedule for the addition of fast-reacting substrate in the on-site pilot plant*

Day	Date	Kraal manure added (L)	Lucerne pellets added (L)
119, 130, 136, 143	12, 23, 29 January, 5 February 2018	240	0
150	12 February 2018	120	120
193, 200	27 March, 3 April 2018	120	0
207	10 April 2018	0	120
223	26 April 2018	120	0
243	16 May 2018	120	120

the ambient temperature, and changes in the substrate replenishment rates.
- Expansion of the assays performed on the samples to include the following: a wide range of metals, sulphide, ammonium, bicarbonate, sodium, potassium, magnesium, chemical oxygen demand (COD), and volatile fatty acids (VFAs).
- Commissioning of the downstream polishing plant to assess the impact on sulphide and manganese removal, and possibly on the reduction in the ammonium, bicarbonate, sodium, calcium, magnesium, phosphate and potassium concentrations, and also of any trace metals that remain in the treated effluent from the BSR process.

Benchmark Costing

A preliminary techno-economic evaluation of passive water treatments was undertaken, consisting of a "benchmarking exercise", by extracting capital and operating costs for passive and semi-passive BSR processes from the literature. Standard cost engineering techniques were applied to bring the costs to a common base of July 2017, and to scale them to a common treatment rate of 1 ML/d, which is envisaged for an industrial-scale operation. Based on this preliminary benchmarking study, the costs for a 1 ML/d passive water treatment plant are estimated to be:

- Capital cost: R25.5-million
- Operating cost: R4.45/m^3 of water treated

An in-house process design and costing package is being developed to produce more accurate costs for the specific passive BSR processes that are under development, utilising local cost data together with the process parameters obtained from the on-site pilot plant operation.

Conclusion

The successful demonstration of a low-cost, low-maintenance passive BSR process during an extended on-site trial will position it for consideration by the coal- and gold-mining industries for the treatment of mine waters emanating from existing processes, and especially after mine closure, producing effluents within regulatory limits specified for discharge or re-use.

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